$Pr(H_3BNMe_2BH_3)_3$ and $Pr(thd)_3$ as volatile carriers for actinium-225. The deposition of actinium-doped praseodymium boride thin films for potential use in brachytherapy

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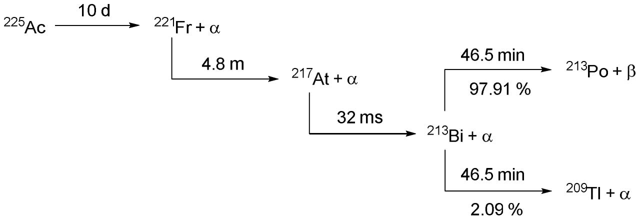
ABSTRACT: Here we show that the praseodymium *N*,*N*-dimethylaminodiboranate complex $Pr(H_3BNMe_2BH_3)_3$ and the 2,2,6,6-tetramethylheptane-3,5-dionate complex $Pr(thd)_3$ can serve as volatile carriers for ^{225}Ac. The actinium coordination complexes $Ac(H_3BNMe_2BH_3)_3$ and $Ac(thd)_3$ are the likely species subliming with the carrier material. A sample of ^{225}Ac-doped $Pr(H_3BNMe_2BH_3)_3$ was used to deposit amorphous ^{225}Ac-doped praseodymium boride films on glass and Si(100) at 300 °C. The alpha emission spectra of the refractory films are well resolved, suggesting that they could be used as radioactive implants for brachytherapy and related treatments.

The high promise of ^{225}Ac for radioimmunotherapy has stimulated research into the fundamental chemistry of actinium[1] and the efficacy of ^{225}Ac conjugates for treating cancer.[2] The ^{225}Ac isotope is desirable for immunotherapy because it has a short half-life (~10 days), and each ^{225}Ac nucleus yields up to four α particles as it decays through the neptunium (4n + 1) decay series (Scheme 1). The resulting α particles have high linear energy transfer (LET) values (60 – 230 keV/μm) and short path lengths in tissue (50 – 90 μm, corresponding to ~2-10 cell diameters), making them ideal for localized treatments. However, preventing the daughter nuclei from entering surrounding tissues remains a challenge; the daughter nuclei often can escape cancer-targeting conjugates due to the high recoil velocity during α emission.[3] One solution to this problem is to encapsulate ^{225}Ac in nanoparticles that prevent the radiotoxic daughters from escaping and circulating freely in the body.[4]

Scheme 1. Radioactive decay chain for ^{225}Ac.

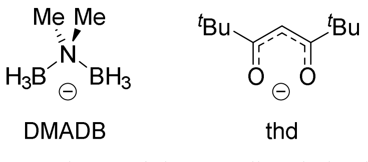


A method to encapsulate ^{225}Ac that has not been widely explored is to embed the isotope in a thin solid film deposited on a surface. Such films would be especially attractive for diffusing alpha-emitter therapy (DART) – a form of brachytherapy that involves implanting alpha-emitting materials into the body to treat cancer and other conditions.[5]

Of the techniques available to deposit thin films, chemical vapor deposition (CVD) is highly attractive because it can provide thin, uniform growth with good adhesion on different substrates with architectures of varying complexity. However, to deposit films containing ^{225}Ac, two requirements must be met: (1) a CVD precursor must be developed to serve as a carrier for ^{225}Ac (i.e., the Ac sublimes with the carrier) and (2) the deposited material must be resistant to chemical etching under physiological conditions.

Only one study of the use of a volatile carrier for Ac has been previously reported: Cp_3Pr (Cp = cyclopentadienyl) was used as a carrier for ^{228}Ac (and also ^{147}Pm) in sublimation processes.[6] These studies provided evidence of the existence of Cp_3Ac and Cp_3Pm, which later were prepared directly.[7]

Chart 1. Structures of DMADB and thd.

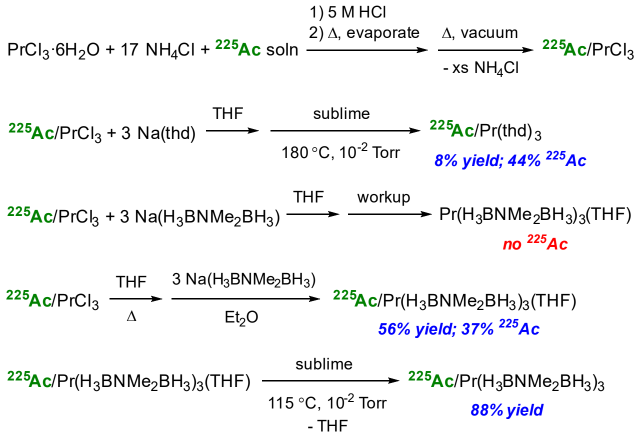


Lanthanide complexes of the *N*,*N*-dimethylaminodiboranate anion (DMADB; Chart 1), such as $Pr(H_3BNMe_2BH_3)_3$, are highly volatile and are useful precursors for the deposition of lanthanide oxide films by CVD.[8] Although to date they have not been evaluated for the deposition of lanthanide boride films, we have shown that other DMADB complexes are effective precursors for the deposition of metal diborides.[9] Refractory metal borides are highly desirable for encapsulating materials because they are inert under physiological conditions. Here we describe the use of the DMADB complex $Pr(H_3BNMe_2BH_3)_3$ and the

2,2,6,6-tetramethylheptane-3,5-dionate complex $Pr(thd)_3$ as volatile carriers for ^{225}Ac, and the deposition of Ac-doped PrB_x films from Ac-doped $Pr(H_3BNMe_2BH_3)_3$. We chose praseodymium as a carrier (rather than other lanthanides) so as to simplify comparisons with the previous study of cyclopentadienyl complexes.

Samples of ^{225}Ac were received as aqueous solutions and used to prepare Ac-doped $PrCl_3$, the anhydrous starting material required for the synthesis of $Pr(H_3BNMe_2BH_3)_3(THF)$ (Scheme 2; CAUTION: proper radiation safety protocols should be followed for handling tracer amounts of alpha-emitters). Aqueous HCl solutions of $PrCl_3 \cdot 6H_2O$ were spiked with 2 - 4 µCi of ^{225}Ac solution. The mixture was evaporated and converted to anhydrous $PrCl_3$ by means of the ammonium chloride method.[10] This approach ensured that the radionuclide was distributed homogeneously in the carrier. Treatment of the ^{225}Ac doped $PrCl_3$ with three equivalents of Na(thd) produced $Pr(thd)_3$, which was isolated by sublimation at 180 °C at 10^{-2} Torr. The recovery of ^{225}Ac in the green sublimate was 44% as judged by comparing the product activity with an equimolar amount of the doped $PrCl_3$ starting material.

Scheme 2. ^{225}Ac/Pr synthesis summary and results.[a]



[a]Percent ^{225}Ac recoveries based on comparison to activity in an equimolar amount of the $^{225}Ac/PrCl_3$ starting material.

For the preparation of the DMADB complex, we found that it was advantageous to pretreat the ^{225}Ac-doped $PrCl_3$ by heating it to reflux in THF, which presumably results in formation of a THF solvate of $^{225}Ac/PrCl_3$, as reported for the synthesis of $PrCl_3(THF)_2$.[11] Treating the isolated THF solvate with three equiv. of $Na(H_3BNMe_2BH_3)$ in Et_2O, followed by extraction and crystallization from pentane, produced green crystals of ^{225}Ac-doped $Pr(H_3BNMe_2BH_3)_3(THF)$.[12] This material was highly active: the net recovery of ^{225}Ac was 37%, which is very similar to the results for ^{225}Ac-doped $Pr(thd)_3$ and the 34% recovery reported for ^{228}Ac using Cp_3Pr as a carrier.[6] The ^{225}Ac-doped $Pr(H_3BNMe_2BH_3)_3(THF)$ was then sublimed at 115 °C at 10^{-2} Torr to afford the corresponding ^{225}Ac-doped and THF-free compound $Pr(H_3BNMe_2BH_3)_3$, as previously described.[8] The presence of the ^{225}Ac dopant in the sublimate was verified using a Geiger counter.

Although obtaining spectroscopic and microanalytical data for ^{225}Ac-doped $Pr(H_3BNMe_2BH_3)_3(THF)$ and $Pr(thd)_3$ was precluded owing to restrictions associated with handling samples containing significant quantities of ^{225}Ac, the properties and physical characteristics of these samples closely resemble those seen for the undoped compounds (solubility, color, sublimation temperatures, and rapid hydrolysis of $Pr(H_3BNMe_2BH_3)_3(THF)$ and $Pr(H_3BNMe_2BH_3)_3$ in water and acid solutions). The results suggest that the actinium complexes $Ac(H_3BNMe_2BH_3)_3$-$(THF)_n$, $Ac(H_3BNMe_2BH_3)_3$, and $Ac(thd)_3$ are generated under the reaction conditions used, and that these species both co-crystallize and co-sublime with their respective praseodymium analogs. After being prepared, both ^{225}Ac-doped $Pr(H_3BNMe_2BH_3)_3$ and $Pr(thd)_3$ were used immediately for deposition studies to avoid further decay loss.

The deposition of ^{225}Ac-doped films from $^{225}Ac/Pr(H_3BNMe_2BH_3)_3$ was conducted in a hot wall CVD reactor in which the substrate was positioned directly above the precursor reservoir (Figure S1; ESI).

Initial control experiments were conducted with undoped $Pr(H_3BNMe_2BH_3)_3$ to test the CVD apparatus and the deposition characteristics of this precursor on glass and Si(100). The substrates were heated to 300 °C and $Pr(H_3BNMe_2BH_3)_3$ was sublimed through the hot zone at 10^{-2} Torr. The resulting shiny black films were characterized by SEM and XPS, which revealed that the morphology and compositions of the films were similar on the two substrates. Because of the hot wall reactor design, more deposition was observed at the bottom of the substrate; this thicker film exhibited some flaking due to stress buildup (Figure 1). However, the film in the middle of the heating zone was smooth and had a thickness of ca. 550 nm as determined by SEM of fracture cross-sections.

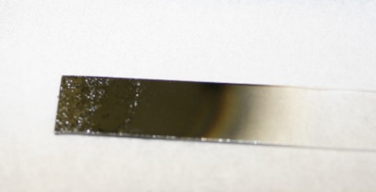


Figure 1. PrB_x film grown on glass at 300 °C using $Pr(H_3BNMe_2BH_3)_3$.

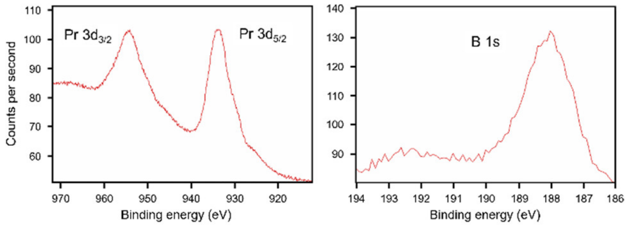


Figure 2. XPS spectra of the PrB_x film on glass.

The SEM micrographs suggested that the films were amorphous, which was confirmed by the lack of peaks in the X-ray diffractograms (Figure S2; ESI). The XPS spectrum showed two peaks 955 and 934 eV corresponding to the praseodymium $3d_{3/2}$ and $3d_{5/2}$ ionizations, respectively, and a peak at 188.1 eV corresponding to the boron 1s ionization (Figure 2).[13] The B 1s binding energy falls within the 187.2 – 189.2 eV range expected for metal boride phases. For comparison, the binding energy for elemental boron is 189.1 – 190.0 eV and for B_2O_3 is 192.2 – 193.5 eV,[13] and the presence of substantial amounts of these phases in the deposited thin film can be ruled out. The ratio of Pr to B for the films according to XPS is 1:5, which does not correspond to either of the two most common praseodymium boride, PrB_6 and PrB_4.[14] Auger spectroscopy data collected as a function of film depth revealed that the Pr/B ratio in the film is uniform (Figure S3; ESI). XPS and Auger spectra also suggest that the films are relatively free of C or N, but there is some oxygen from post-growth oxidation, as is typically seen (see ESI).

As expected for metal boride films, which generally are oxidation and corrosion resistant, the films do not hydrolyze to any significant extent in air or water, and they are only slowly etched over several days when immersed in 12 M HCl, as shown by the fact that the films remain dark and resist dissolution under these conditions.

Depositions from ^{225}Ac-doped $Pr(H_3BNMe_2BH_3)_3$ were conducted in the same way as described above for the undoped samples. The resulting film had the same characteristics as the undoped films and similar XPS spectra (Figure S4; ESI). The EDS spectra did not show clear evidence of Ac in the film (as expected for the trace concentrations present; emissions observed near 3 keV are due to background argon), but the α spectrum revealed the diagnostic α energy distributions for ^{225}Ac and its decay daughters ^{221}Fr and ^{217}At (Figure 3). The α emission peaks are well resolved with only a small amount of tailing due to inelastic scattering effects, indicating that the films are thin and uniform.[15] The film emits ca. 0.42 Bq (11 pCi) of α-particles; the activity can easily be adjusted to any desired value by dosing the carrier with the appropriate amount of ^{225}Ac.

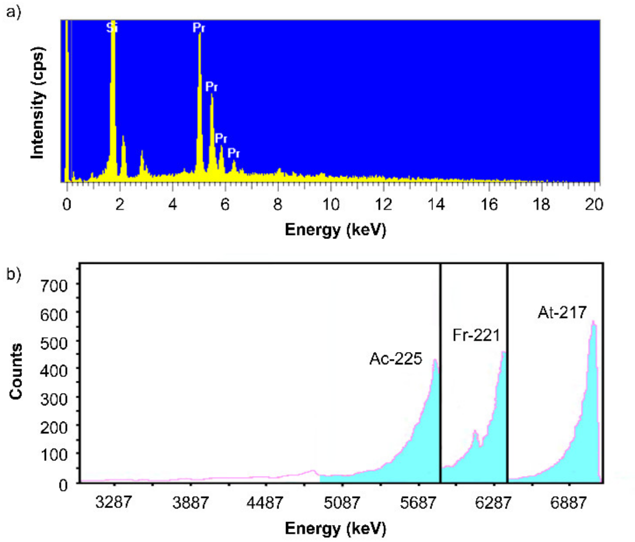


Figure 3. EDS spectrum (a) and alpha spectrum (b) of the ^{225}Ac-doped PrB_x film grown on glass at 300 °C from $^{225}Ac/Pr(H_3BNMe_2BH_3)_3$. The lines and cyan shading in the alpha spectrum represent integration endpoints for each radionuclide. Integration values are tabulated in the ESI.

The deposition of ^{225}Ac-doped PrB_x films demonstrates that volatile lanthanide precursors can be used as carriers for Ac in CVD processes. The co-crystallization and co-sublimation of ^{225}Ac with the Pr carriers suggest that Ac forms compounds of stoichiometry $Ac(H_3BNMe_2BH_3)_3(THF)_n$, $Ac(H_3BNMe_2BH_3)_3$, and $Ac(thd)_3$, and that the first of these compounds is soluble in pentane and the latter two are volatile. The ^{225}Ac-doped PrB_x films deposited by using $Pr(H_3BNMe_2BH_3)_3$ as a carrier provide the first "proof-of-concept" that ^{225}Ac-doped films, deposited on a biocompatible substrate, are potentially useful for applications such as brachytherapy. The films are thin enough that the alpha particles can escape to irradiate surrounding tissue, as determined by the relatively high resolution of the alpha energy spectrum. The refractory boride films are chemically inert and are etched only under highly acidic conditions, which would not be encountered *in vivo*. It is likely that the film matrix prevents the loss of daughter radionuclides into the surrounding environment; this attribute would be a significant advantage over other radioimmunotherapy treatment regimens. The results suggest that ^{225}Ac-doped PrB_x films could be useful as implants for diffusing alpha-emitter radiation therapy.

ASSOCIATED CONTENT

Supporting Information. Experimental, details of the CVD reactor, Auger and XPS data, and tabulated alpha spectrum data. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

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(12) We have previously shown that $LaCl_3$ and $CeCl_3$ do not react with $Na(H_3BNMe_2BH_3)$ in thf to afford the corresponding $M(H_3BNMe_2BH_3)_3(THF)$ complexes (see ref. 8); if this lack of reactivity arises because these two lanthanides have large ionic radii, then one might have expected $AcCl_3$ (which has an even larger radius) would likewise not generate the desired complex under these conditions. But dispersal of the actinium in the more reactive $PrCl_3$ matrix would account for the success of the salt elimination reaction.

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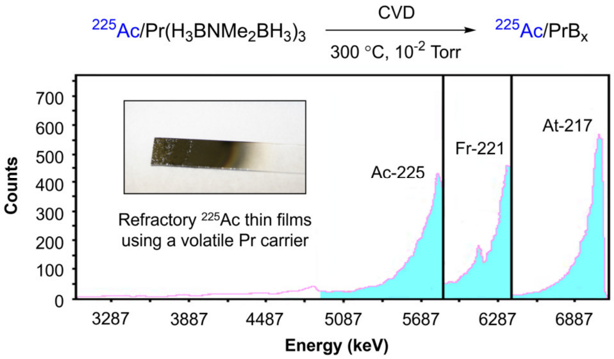
SYNOPSIS TOC. This paper shows that two volatile praseodymium complexes can serve as volatile carriers for ^{225}Ac, and that one of them can be used to deposit amorphous ^{225}Ac-doped praseodymium boride films. The alpha emission spectra of the refractory films suggest that they could be used as radioactive implants for brachytherapy and related treatments.



^{225}Ac/Pr(H$_3$BNMe$_2$BH$_3$)$_3$
CVD
300 °C, 10^{-2} Torr
^{225}Ac/PrB$_x$
Refractory ^{225}Ac thin films using a volatile Pr carrier
Ac-225
Fr-221
At-217
Counts
0
100
200
300
400
500
600
700
3287
3887
4487
5087
5687
6287
6887
Energy (keV)